SUSTAINABLE HYDROGEN FROM BIO-OIL - CATALYTIC STEAM REFORMING OF ACETIC ACID AS A MODEL OXYGENATE

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Introduction

Hydrogen as a fuel has recently been an important issue due to developments in fuel cell technology. Hydrogen production from sustainable sources, e.g. biomass, is gaining attention for a CO_2 neutral energy supply. Recent developments in flash pyrolysis technologies make it possible to convert lignocellulosic biomass efficiently to a bio-oil, which is easier for handling and transport.[1] The bio-oil so generated contains a variety of aliphatic and aromatic oxygenates (aldehydes, ketones, acids, alcohols).

Combination of catalytic steam reforming and water gas shift reaction is the most promising option to generate hydrogen since these reaction steps maximize hydrogen yield. During steam reforming of bio-oil, deactivation due to coke/oligomer deposition on the catalysts is a severe problem. It has been reported[2] that deactivation is unavoidable even in the presence of excess steam ($H_2O/C > 5$). Economically, lower steam/carbon (S/C) ratio (< 2) is preferable. In this study, Pt/ZrO_2 has been investigated since earlier work [3] has shown excellent activity and stability for Pt/ZrO_2 under conditions favorable for coke formation, for e.g., even in the absence of steam, during CO_2 reforming of natural gas.

Bio-oil is a mixture of oxygenates. In order to provide a knowledge base for the design of active and stable catalysts for steam reforming of bio-oil, studies have been initiated with model oxygenates. Acetic acid (HAc) has been chosen as a model compound in this study because it is a major component of bio-oil (up to 32 wt%).[1] It is known that steam reforming and water gas shift reaction ($CO + H_2O \rightleftharpoons CO_2 + H_2$) occur simultaneously and the overall stoichiometry is represented (Equation 1),

$$CH_3COOH + 2H_2O \rightarrow 2CO_2 + 4H_2 \quad \ldots(1)$$

This study describes attempts to understand the reaction and deactivation mechanisms in order to establish guidelines for the design of efficient catalysts for steam reforming of bio-oil.

Experimental

Catalyst preparation. Pt/ZrO_2 was prepared by wet impregnation technique[3]. Pt loading was set to 0.5 wt%. The catalyst was calcined at 925 K for 15 h.

Catalytic measurements. The amounts of 50 mg of catalysts were loaded in a fixed bed reactor and held by quartz wool plugs. The catalyst was first reduced in 5% H_2 in N_2 at 925 K fir 1 hr. An aqueous solution of HAc giving a steam to carbon molar ratio (S/C) of 5 was introduced by using a microfeeder (KD Scientific) and a syringe (Hamilton co.). Gas mixture, $HAc/H_2O/N_2/Ar$, was fed to give a ratio of 3/30/5/82 ml min^{-1} (N_2 as an internal standard). For analysis, a flame ionization detector (FID) and a Hayesep Q column were used for HAc, acetone, ketene, and hydrocarbons; a thermal conductivity detector (TCD) and a Carbosieve column were used for H_2, N_2, CO, CH_4, and CO_2.

Pulse experiments were performed with 20 mg of Pt/ZrO_2. After reduction at 925 K, the system was purged in Ar at a flow rate of 37.5 ml min^{-1}. Pulses of HAc aqueous solution (S/C = 5, 3.5 μmol of HAc) at 293 K were introduced.

The hydrogen yields were calculated based on Equation 1. For carbon containing compounds, the yields were calculated based on C1 equivalent values.

Catalyst characterization. Thermogravimetry (TG) (Mettler Toledo TGA/SDTA 851E) was used to determine the amount of deposits in the catalysts.

IR spectra were recorded *in situ* under vacuum in transmission mode (Bruker, Vector 22, MCT detector). The catalyst reduced *ex situ* at 925 K was mounted in the IR cell and firstly reduced *in situ* by introducing 0.1 mbar of H_2 at 725 K. After evacuation, oxygenates and steam were introduced into the system with an S/C molar ratio of 5 at a total pressure of 0.1 mbar at 725 K. Each spectrum consists of 32 scans taken at 4 cm^{-1} resolution.

Results and Discussions

Figure 1 shows HAc conversion and yields of products during HAc/H_2O reaction over Pt/ZrO_2. Conversion was close to 100% and constant for 3 h, however, yields of products changed with time. In the beginning (5 min), H_2 and CO_2 were the main products, CH_4 and CO were observed in small quantities. H_2 yield (47%) was close to equilibrium value (56%). The product yields and pattern indicates that the catalyst was active for steam reforming However, after 25 minutes time on stream, H_2 and CO_2 yields decreased drastically, and an increase in acetone was observed.

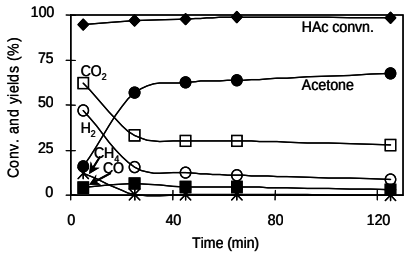

Figure 1. Conversion and yields for steam reforming of HAc over Pt/ZrO_2 catalyst. (725 K, S/C = 5, GHSV = 160000 h^{-1}).

Figure 2 shows HAc conversion and yields of products during HAc/H_2O reaction over ZrO_2 (without Pt). HAc conversion was close to 90%. The conversion of HAc and yields of the products were constant for 3 h. However, no steam reforming activity (H_2 and CO) was observed, and only acetone and CO_2 were observed as products. HAc is known to convert to acetone easily and the reaction is catalyzed by a variety of oxides.[4] ZrO_2 is also known as such an oxide. The stoichiometry of the products observed (acetone and CO_2, 1:1) correspond to the ketonization reaction (Equation 2).

$$2CH_3COOH \rightarrow CH_3COCH_3 + CO_2 + H_2O \quad \ldots(2)$$

Both Pt/ZrO_2 and ZrO_2 were very active for HAc conversion. However, H_2 and CO, i.e., steam reforming products were produced only over Pt/ZrO_2 and not over ZrO_2. This implies that presence of Pt is essential for steam reforming. ZrO_2 shows acetone yields similar to those observed over Pt/ZrO_2 after 25 minutes time on stream (Figure 1), indicating that even after the active sites for steam reforming were deactivated, the accessible ZrO_2 sites still provided the activity to form acetone and CO_2.

For Pt/ZrO_2 and ZrO_2, TG experiments showed approximately 1.2 and 0.8 wt% deposits, respectively, after 3 hour test. Regeneration in air restored catalytic activity, indicating that blocking active sites by deposits caused deactivation of the Pt/ZrO_2 catalyst for the steam reforming.

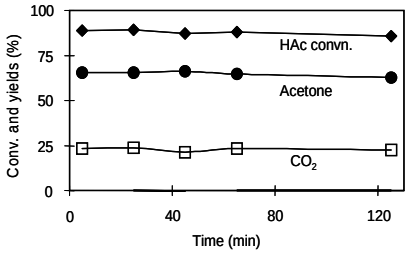

Figure 2. Conversion and yields for steam reforming of HAc over ZrO_2 catalyst. (725 K, S/C = 5, GHSV = 160000 h^{-1}).

Presence of acetone in the product mixture and formation of deposits on ZrO_2 indicates a role for acetone in catalyst deactivation. Acetone is known to undergo aldol type condensation and give products such as diacetone alcohol, mesityl oxide (MO) and MO is known to form oligomers easily ($CH_3COCH_3 \rightarrow (CH_3)_2C(OH)CH_2COCH_3 \rightarrow (CH_3)_2C{=}CHCOCH_3 \rightarrow$ oligomers).[5] In order to check if these oligomers play a role in deactivation, kinetic and *in situ* IR measurements were carried out with Pt/ZrO_2 pre-exposed to MO.

Table 1 shows comparison between HAc conversion and H_2 yield with or without MO treatment during pulse experiment. It is seen that Pt/ZrO_2 catalyst deactivated for H_2 formation (steam reforming) more rapidly when contacted with MO in comparison to HAc.

Table 1. Comparison of HAc Conversion and H_2 Yield between Fresh and MO Treated Pt/ZrO_2

Catalyst (Pt/ZrO_2)	HAc convn. (%)	H_2 yield (%)
Fresh	98.2	60.0
MO treated[a]	82.4	29.1

[a]MO/H_2O pulse (0.32 µmol-MO, S/C = 5) was introduced before a HAc/H_2O pulse.

In situ IR spectra recorded over Pt/ZrO_2 are shown in **Figure 3**. In the presence of HAc/H_2O (**Figure 3a**) characteristic peaks for linear CO adsorbed on Pt at 2060 cm^{-1} were observed. This confirms the production of CO in the *in situ* experiment. Additionally bands due to oxygenates (acetate, carbonate) derived from HAc (1541, 1426 and 1405 cm^{-1}) were also seen. Exposure-evacuation cycles with HAc/H_2O were repeated three times (not shown) and no significant difference in IR spectra were observed.

After pre-exposure to MO, *in situ* IR spectra were recorded with HAc/H_2O (**Figure 3b**). The spectra showed similar oxygenate peaks on the support but the CO peak was very weak. This implies the activity towards CO formation (steam reforming) was deactivated as expected from kinetic experiments. However, when CO was introduced in the gas phase, the intensity of the peak for CO significantly increased (**Figure 3c**). This indicates that the Pt surface was not blocked completely even though the activity for steam reforming was lost. This further implies that only part of the surface Pt atoms are responsible for steam reforming. Since oligomerization reactions of MO occur on the support, and the fact that Pt sites were deactivated with MO, we conclude that the Pt sites active for steam reforming are at the close vicinity of the support. This is in agreement with a bi-functional mechanism proposed by us for the steam or CO_2 reforming of methane, where methane is activated on the metal and steam or CO_2 on the support, the reaction occurring at the metal support boundary.[3,6] Thus, ZrO_2 may have a key role in the mechanism for steam reforming in the activation of water. Once MO, or the oligomers derived from it, is formed on the support even in small amounts, they could block the boundary sites and deactivate the Pt/ZrO_2 catalyst.

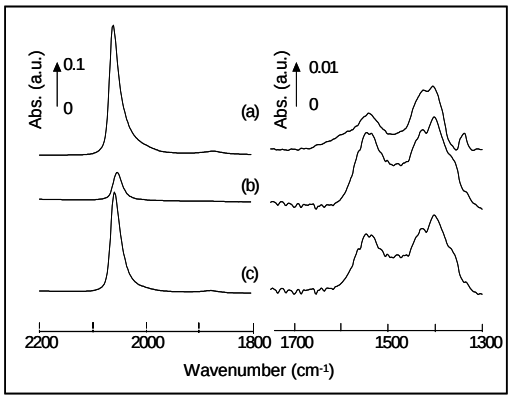

Figure 3. *In situ* IR spectra over Pt/ZrO_2 at 725 K (Steam/Carbon = 5, 0.1 mbar). (a) HAc/H_2O, (b) HAc/H_2O after MO/H_2O treatment and evacuation, (c) CO treatment after (b) without evacuation

The acid-base properties of the support oxides play a key role in catalyzing the condensation reactions.[5] ZrO_2 has an important role in steam reforming *via* steam activation. However, condensation reaction could also happen over ZrO_2. Thus, design of a stable catalyst should be aimed at improvement of the support, minimizing the condensation reactions as well as enhancing the steam activation capacity.

Conclusions

The Pt/ZrO_2 catalysts showed high activities at initial time on stream, but lost its activity for steam reforming (H_2 production) rapidly.

Results obtained in the study point to a bifunctional mechanism for steam reforming of HAc on Pt/ZrO_2, i.e., HAc activation takes place on Pt and steam activation on ZrO_2. The reaction occurs at the Pt periphery in close proximity of ZrO_2. The catalysts deactivate due to blocking of active sites by oligomers derived from HAc/acetone on ZrO_2. In order to develop a durable catalyst, the oligomerization/condensation reactions which take place on the support need to be minimized.

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